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CONVERSION OF CATTLE FEEDLOT WASTES TO AMMONIA SYNTHESIS GAS

TEXAS TECH UNIVERSITY

PREPARED FOR
ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY

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By

James E. Halligan
Karl L. Herzog
Harry W. Parker
Robert M. Sweazy
Department of Chemical Engineering
and
Water Resources Center
Texas Tech University
Lubbock, Texas 79409

Grant No. R801065
Program Element 1BB039
ROAP 21-BES Task 031

Project Officer

R. Douglas Kreis
Robert S. Kerr Environmental Research Laboratory
National Environmental Research Center
P. O. Box 1198
Ada, Oklahoma 74820

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ABSTRACT

A study was undertaken to determine the potential of a process to convert cattle feedlot manure into anhydrous ammonia. Due to the fact that ammonia is currently produced on a large scale using natural gas and air, only the processing associated with a reactor system to convert the manure into a suitable synthesis gas was considered in this study. The synthesis gas can be further processed to anhydrous ammonia using existing technology.

During this phase of the project, a 4.1-cm diameter fluidized-bed reactor system was designed, constructed, and operated. Significant yields of synthesis gas were obtained when this system was fed a mixture of manure, air, steam, and a very small stream of carbon dioxide. This synthesis gas was deemed to be compatible with existing ammonia plant technology and suitable for subsequent conversion to anhydrous ammonia. The upper limit of the production rate of this gas was not determined in this study; however, the ammonia equivalent of manure was shown to be in excess of one-half metric ton of ammonia per metric ton of dry, ash-free animal waste. Assuming that on an as-is basis the manure contained 15% moisture and 25% ash, this would translate to approximately 317 kg of ammonia per metric ton of manure received.

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SECTION I

CONCLUSIONS

1. For a 4.1-cm in diameter fluidized-bed reactor system similar to that used in this study, the partial oxidation of cattle feedlot manure, if followed by conventional desulfurization and reforming steps, can result in a synthesis gas suitable for the production of anhydrous ammonia.

2. An upper limit for the synthesis gas production rate was not observed over the temperature range investigated in this study; however, the ammonia equivalent of the reactor gases was shown to be in excess of one-half metric ton of ammonia per metric ton of dry, ash-free animal waste. Assuming that on an as-is basis a manure contained 15% moisture and 25% ash, this would translate to approximately 317 kg of ammonia per metric ton of manure received.

3. Tentative energy balances indicate that the partial oxidation step of a synthesis gas from manure process would require the addition of little or no chemical and latent energy. However, sensible energy conservation would be required to make the step adiabatic unless the energy in the char were to be recovered.

4. At a mean reactor temperature of 800° C, approximately 18% of the carbon in the manure feed exited the reactor as char. This char was 54% by weight ash and had a heating value of 2290 cal/gr. On a dry mass basis, approximately 22% of the manure fed to the reactor exited in the char stream. Due to the large steam demands associated with an ammonia plant, this material can probably be used for boiler fuel. However, disposal of the ash will still be required. If no other suitable use is developed, this material could be used for landfill.

SECTION II

RECOMMENDATIONS

1. A larger scale reactor system should be built in order to establish a design basis for a metric tons-per-day scale plant.

2. The temperature within the reactor should be increased in an effort to determine the limiting synthesis gas yield.

3. The new reactor system should be constructed with pressure-holding fittings which would allow investigations at modest pressures.

4. Electrostatic precipitators should be added to the reactor system to allow greater closure of material and energy balances.

5. The future fluidized-bed system should have provision for char removal by some means other than entrainment so that superficial velocities within the reactor can be lowered.

6. The development of technology compatible with or downstream of a manure to anhydrous ammonia should be carefully monitored. Programs are underway to remove sulfur from power gas at elevated temperatures and to utilize the ash from cattle feedlot manure. Careful monitoring will insure that developments within this project are consistent with objectives within those programs.

SECTION III

INTRODUCTION

Approximately 25 million head of feedlot cattle are marketed annually to supply the beef demands of the United States.[1] The most negative aspect of feedlot operations is the animal waste, particularly the manure which can harm the environment through the watershed and through the atmosphere.[2] When cattle are fattened by grazing, the large area of land involved dilutes the effects of pollution, but this is not so at the feedlot. Land spreading, still the most used method of manure management,[3] cannot be economically attractive when large quantities of manure must be trucked any distance to achieve dilution. Great piles of manure beside the feedlot result.

The trend toward large feedlots[1] is evidenced by the High Plains of Texas where in the Hereford-Dimmitt area the estimated capacity of 30 lots is in excess of 800,000 head.[4] Such large numbers of cattle require that many thousands of acres be in grain crops. In turn, these crops require such fertilizers as anhydrous ammonia. Therefore, large ammonia plants are not uncommon in the vicinity of extensive, fed-cattle operations.

Most of the ammonia produced in the United States is based on reforming natural gas with steam to produce the hydrogen-nitrogen mixture required for ammonia synthesis.[5] Because the present critical shortage of

natural gas may develop into a disastrous shortage, many ammonia producers are making provisions to replace natural gas with other hydrocarbons for various fuel requirements.[6] Obviously, the energy situation would not preclude the complete elimination of natural gas if cheaper sources of synthesis gas could be made available. During the course of this project, we have been seriously contacted by more than six firms relative to the commercialization of this project.

Halligan and Sweazy[7] have compared previously proposed conversions of solid waste to methane[8] and to oil with their own concept of ammonia synthesis gas from cattle manure. Their estimates show that each of these three conversions would have a product value of about $9,000 per day given 1900 metric tons of manure, the estimated daily production of 600,000 cattle. However, due to its relative simplicity and its obvious consistency with the economy of cattle-producing areas, the conversion to ammonia synthesis gas appeared to be the most attractive for future development.

The thermochemical calculations made by Halligan and Sweazy were for the conversion of manure to a gas containing H_2 and CO together in a 3:1 molar ratio with N_2. This gas mixture would be suitable as feed to the shift converters preceding an ammonia synthesis loop. The nitrogen required in the synthesis was to be provided by adding air to a manure pyrolysis reaction. Although the addition of air would result in energy release through partial oxidation of the manure, the overall step to synthesis gas was shown to be endothermic. The continuous reaction scheme and the fast-heating environment operative within a fluidized bed led to the selection of this technology for application to the partial oxidation of manure.

As envisioned by Halligan and Sweazy,[7] ammonia synthesis gas, a relatively pure mixture of hydrogen and nitrogen, would be produced, at least in

part, by the partial oxidation of the animal waste with air. Partial oxidation is intermediate to pyrolysis and combustion, the two extremes of thermochemical processing. Pyrolysis is simply the thermal decomposition of an organic material in the absence of oxygen. When less than stoichiometric quantities of oxygen are added to a pyrolysis reaction, a partial oxidation, or partial combustion, of a portion of the pyrolysis products occurs.

The results of any reported thermochemical processing of manure are subject to many variables and must be interpreted with care. Although the dry, ash-free portion of cattle manure is composed largely of cellulose, hemicellulose, lignin, and ligno-protein complexes,[10] the relative amounts of these constituents depend on the feed ration.[11] Therefore, the temperature range in which exothermal decomposition begins, as well as the yields and compositions of the gases, liquids, and chars resulting from pyrolysis, can differ substantially from one of these natural polymers to the other.[12] The reactions involved in the pyrolysis and combustion of cellulose alone have been found to be influenced by the temperature and the period of heating, by the supply of oxygen, steam, and other reacting or inert gases, and by the presence of inorganic impurities.[13] Despite the complexity of the situation, trends can be gleaned from the literature. Albeit with different goals and intentions several groups of investigators have conducted batch pyrolyses of manure.

White and Taiganides[14] performed laboratory-scale batch pyrolyses of beef, dairy, swine, and poultry manures in an effort to establish the heating value of the gaseous products. Samples were heated at controlled rates to 800° C at which temperature the retort was maintained until gas evolution ceased. The gas included H_2, CO, CO_2, combustibles (methane and ethane), and illuminants (olefins and aromatic hydrocarbons). The gas from beef manure contained an average of 1206 kg cal/kg

of combustion energy per kg of dry, volatile solids charged. No detailed analyses were performed on the manure samples or on the residual chars and liquids.

In an effort to maximize yields of liquid organic compounds, Garner and Smith[11] conducted a series of batch pyrolyses of steer manure. Using thermogravimetric analysis and differential thermal analysis to identify a temperature range for conducting the pyrolyses and employing Evolutionary Operation to guide the experiments, these investigators determined that low pressures and maximum temperature of 400° to 500° C were optimum for the production of liquid products.

Due to the estimated high costs for separating the complex liquid pyrolysate, which included alcohols, aldehydes, ketones, acids, amines, and phenols, into its components, the authors ruled out manure pyrolysis for the value of the liquids. Estimated costs for predrying the manure, which was assumed to be 80% moisture, were also prohibitive. It should be interjected that Halligan and Sweazy[7] had previously discounted a solid waste-to-liquid conversion which would require few separation steps, the cellulose-to-oil scheme proposed by Appell and others.[9] Garner and Smith concluded their studies with a simulated, continuous pyrolysis at 500° C and atmospheric pressure. A purge stream of helium was passed through the retort to rapidly remove the primary products of pyrolysis and minimize secondary reactions. The results of this experiment have been summarized in Table 1.

At the Bureau of Mines, Schlesinger and others[15] pyrolyzed feedlot manures under batch conditions with a terminal temperature of 900° C. These investigators were interested in converting agricultural wastes to gas, liquid, and low volatile solids to facilitate incineration. The authors reported that the volatile material was reduced from 66.5% in the manure charged to 2.7% in the char. A summary of this pyrolysis has also been included in Table 1.

Table 1. SUMMARY OF REPORTED BATCH PYROLYSES OF MANURE

	Investigator	
	Garner and Smith[11]	Schlesinger and others[15]
Temperature	500° C	900° C
Analysis of dry manure (weight percent)		
Carbon	-	42.7
Hydrogen	-	5.5
Oxygen	-	31.2
Nitrogen	-	2.4
Sulfur	-	0.3
Ash	9.2	17.8
Yields (weight percent dry, ash-free feed)		
Gas	22.7	48.6
Ash-free char	29.2	23.6
Liquid organics	23.7	7.3
Aqueous phase	18.4	20.1
Gas composition (volume percent)		
H_2	11.0	27.5
CO	20.4	18.0
CO_2	49.6	24.5
CH_4	16.4	22.7
C_2^+	2.7	7.3

Garner and Smith minimized the production of gas by purging the retort with helium, while in the Bureau of Mines pyrolysis there was no purge with inert gas; therefore, high temperature can be inferred as important in maximizing gas and minimizing organic liquids and char. The importance of high temperatures and heating rates for attaining high yields of gas from cellulosic materials has been stressed elsewhere.[16, 17] As gas yields will undoubtedly be of importance in establishing the feasibility of synthesis gas from manure, continuous reaction schemes that employ fast-heating environments appear to be the most promising for future study.

Moving beds have been used in the gasification of coal.[18] The principal advantages of moving beds are maximum heat economy and, for coal, a high conversion of the solid to gas. At Texas Tech University the mechanical feasibility of a moving-bed, solid-waste retort has been established with manure as the feed.[19, 20] This unique retort operates in a two-step cycle involving partial oxidation and pyrolysis. The manure undergoes drying, heating, pyrolysis, partial oxidation, and, finally, cooling as it moves down the reactor. In the pyrolysis zone, the manure is heated slowly at temperatures no greater than 427° to 538° C resulting in relatively high yields of liquid organics (13.2 kg/ 45.4 kg dry, ash-free manure fed). A moving bed appears, then, to create less than the best conditions for high gas production from a highly volatile material such as manure.

Rapid heating is one of several unique features of the fluidized bed that has prompted the application of this technology to the pyrolysis and incineration of solid wastes.[17, 21, 22, 23] Additional features include: efficient gas-solid contact and extended particle surface which result in high specific gasification rates; rapid solids backmixing which creates a thermal flywheel and which would facilitate the

processing of materials with varying moisture content and composition; and simple construction involving no internal parts. These aspects make the fluidized bed a potentially attractive means for effecting the partial oxidation of manure. Historically, the first commercial application of the fluidized bed was the Winkler process for producing raw synthetic gas from brown coal via partial oxidation.[24]

Bailie[25] and other investigators[26, 27] have used bench-scale fluidized beds, such as the one employed in this work, to combust manure. In the 38.1-cm diameter, fluidized bed used in the Bailie study, the bed material was sand fluidized with a preheated gas mixture of nitrogen and carbon dioxide containing traces of oxygen. At a feed rate of 11 kg/hr of wet manure (7.8% moisture) and at a bed temperature of 760° C, the gas generation was 280 ℓ/0.454 kg of dry manure fed. The pyrolysis gas had the following composition: 31% H_2, 38% CO, 20.6% CO_2, 7.7% CH_4, 1.9% C_2H_4, and 0.3% C_2H_6. The mass of gas evolved represented 73% of the mass of the dry, ash-free manure fed to the bed.

SECTION IV

EXPERIMENTAL EQUIPMENT, PROCEDURES, AND MATERIALS

This section includes a description of the laboratory-scale facility for the gasification of manure, recounts operating and analytical procedures, and characterizes the manures fed in the partial oxidation studies.

EQUIPMENT

The flow diagram of the bench-scale apparatus is shown in Figure 1. Central was the fluidized bed reactor which was constructed from 3.8 cm, Schedule 40, Incoloy 800 pipe to permit operation at temperatures up to 87° C. The reactor was partially enclosed by a 1000-watt tubular Hoskins Type FH305 Electric Furnace to supply heat for endothermic reactions and to compensate for heat losses.

Reactor details are given by the cross-sectioned view of Figure 2. The fluidizing airstream mixture entered the conical base section of the reactor through a 1.7-cm outside diameter (OD) Incoloy tube. The reactor contained two 0.32-cm diameter, swaged magnesia, Type K thermocouples. The sheath of the lower thermocouple came up through the gas inlet and coincided with the center line of the 4.06-cm inside diameter (ID) reactor. The Chromel-Alumel junction of this thermocouple was 13.46 cm above the reactor base, while the upper thermocouple junction was situated 3.05 cm below the entrance to a 1.27-cm OD Incoloy dip tube which

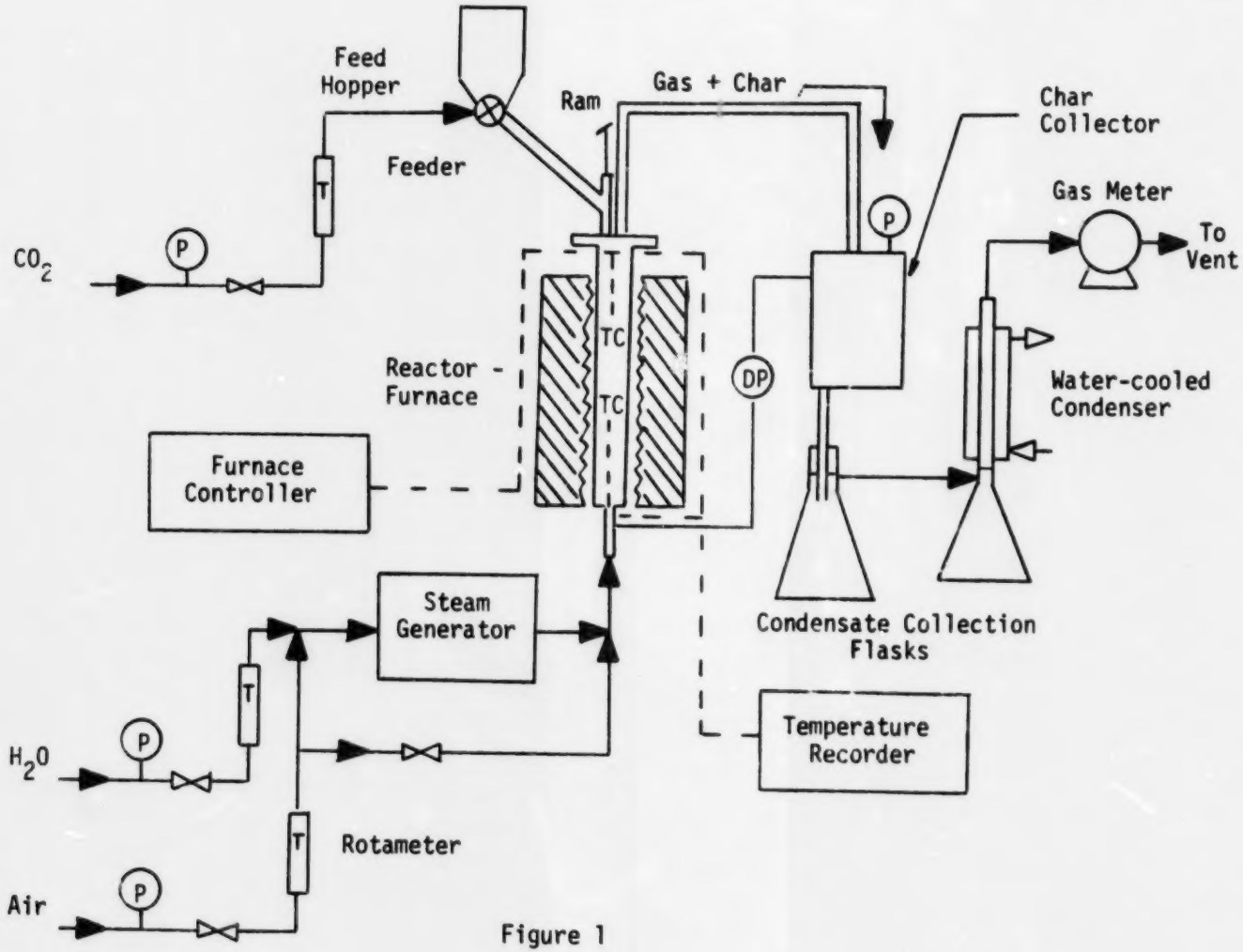


Figure 1

Partial oxidation of manure - flow diagram

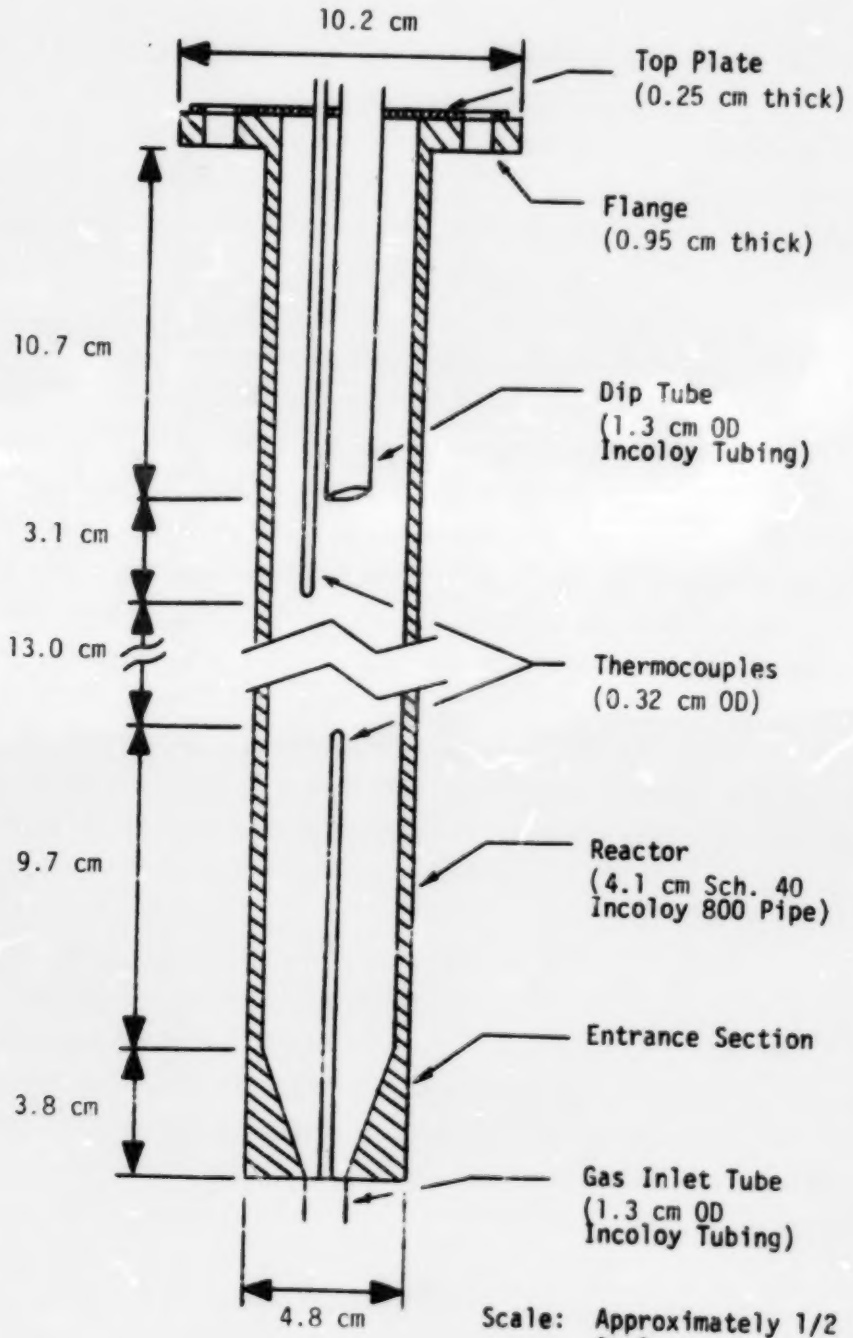


Figure 2

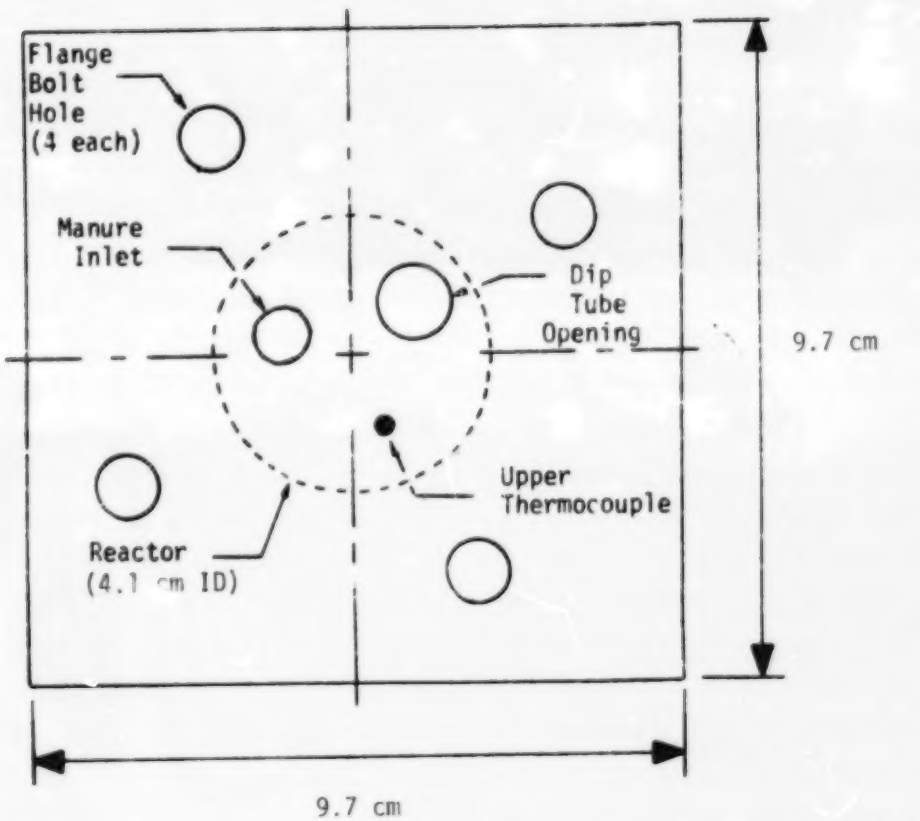
Reactor details

provided an exit for the product gases and for the reacted solids by entrainment. Each thermocouple was connected to four points of a twelve-point Honeywell temperature recorder with a range 0° to 1200° C. The upper thermocouple served as the sensor for a Thermoelectric Model 32422 Indicating Thermocouple Controller which regulated the power to the furnace.

The reactor contained no inlet gas distributor because its initial design and operation called for bottom feeding in which manure was transported by the fluidizing gas up into the bed. However, this mode of feeding was abandoned due to frequent plugging of the transport line. In the top feeding arrangement shown in Figure 1, manure was allowed to fall by gravity from a star-type solids feeder, driven by a variable-speed Bodine gear motor, directly into the top of the reactor. A small, metered stream of carbon dioxide was passed through the manure feed line to prevent condensibles, such as steam, from back-flowing in this line and creating plugging problems. A manually-operated ram was installed so that the vertical section of the feed line could be cleaned of plugs and deposits during a run. Figure 3 shows the positioning of the manure inlet, the dip tube, and the upper thermocouple with respect to the reactor center line.

Other equipment items included a steam generator which was simply a copper box in an electric furnace. A portion of the air feed was passed through the steam generator to provide smooth vaporization. The total air rate, as well as the CO_2 rate to the manure feed line, was indicated and maintained at the preset level by a Brooks-Sho-Rate Rotameter equipped with an integral flow controller.

Downstream from the reactor was a char collector which employed velocity reduction to separate the reacted solids from the gas stream. A Magnehelic gauge with range 0 to 12.7 cm of water gave the differential pressure between the gas inlet to the reactor and the char collector.



Scale: Approximately Full Scale

Figure 3

Top plate of reactor, bottom view

Two air-cooled flasks followed the char collector to receive condensing steam and organic vapors. A water-cooled condenser dried the gas to its saturation level before it exited through a Precision Wet Test Meter to vent.

OPERATIONAL PROCEDURE

A partial oxidation run was initiated by bringing the empty reactor up to temperature with air and steam alone flowing. A small back pressure was temporarily imposed on the system to insure the absence of leaks. Manure feeding was begun, and the system was allowed to reach a steady state as determined by the leveling of the reactor temperatures. This leveling period normally required about 30 minutes. The char and condensate collectors were then emptied and a material balance period was begun. During the course of the next one to two hours, exit gas rates were determined and recorded. Gas samples were taken with 50-ml syringes at a point just upstream from the wet test meter. Although the manure feeder was roughly calibrated for the milled particles fed, the manure rate was determined using the run time and the difference between the initial and the final weights of the feed hopper. Likewise, the total condensate rate was determined by the increase in the weights of the condensate flasks over the material balance period. The char collector was dumped and thoroughly brushed to obtain the entire solids production of a period.

A Carle Model 8000 Basic Gas Chromatograph, equipped with a Carle Number 6547 Oxidation Gas Analysis Package, was used to routinely analyze gas samples. With helium carrier gas flowing at 40 ml/min and with a column temperature of 38° C, this thermal conductivity chromatograph separated O_2, N_2, CO_2, CH_4, C_2H_6, C_2H_4, and CO in less than 10 minutes. Mixtures of these gases were made and peak height versus volume percent calibration curves were prepared for each specie. The chromatograms were given by a Sargent Model SR strip chart recorder.

The water content of a gas sample was estimated by assuming that the partial pressure of the water was equal to its vapor pressure at the ambient temperature. The percentage of H_2 in a gas sample was estimated by the difference between the total volume and the volume of gas unaccounted for by this analysis. This differencing technique was tested by using the Carle chromatograph but with nitrogen as the carrier gas to determine the hydrogen concentration of some duplicate samples taken in a preliminary run. Using the estimated water vapor content, from 97% to 98% of the gas could be accounted for by the two analyses, indicating that, when the actual percentage of hydrogen is 20, the percentage determined by difference would be from 22 to 23. This accuracy was deemed to be sufficient for the purposes of this study.

In two runs, a Unico Precision Gas Detector fitted with Kitagawa Detector Tubes, Catalog Number 120a, was used to determine the concentration of H_2S in the gas exiting to vent.

The chars and the manures fed were characterized as to moisture content, ultimate analysis, and heating value. The moisture content of a solid sample was determined by the weight loss upon drying overnight at 102°-103° C. A Hewlett-Packard Carbon-Hydrogen-Nitrogen Analyzer was employed to obtain an elemental analysis exclusive of oxygen. The reader is referred to the C-H-N Manual[28] for the details of this technique. The ash content of a sample was taken as the material remaining upon ignition in a muffle furnace at 750° C. A Parr Peroxide Bomb Calorimeter was used to determine the thermal values of manure and char samples. The use of this instrument followed the operating instructions given by Parr.[29] As recommended in the instruction manual, a hydration correction of 0.111° C per gram of sample charged to the bomb was assumed in calculating all heats of combustion. A Parr Turbidimeter was used to obtain the total sulfur content of manure samples.

The chemical oxygen demand and the total, volatile, and fixed residues of a condensate were obtained by the techniques described in Standard Methods.[30]

FEED MATERIALS

The cattle manures used as feeds in the partial oxidation studies were obtained from the nearby Texas Tech experimental feedlots. Two batches, hereafter designated as Manure "A" and Manure "B", were collected. Each batch was milled so as to completely pass a No. 40 USS Sieve. The -40 +60 portion was retained as feed material. Samples in this particle-size range were taken for the solids characterizations described in the preceding section. Table 2 presents the results of these tests. Also presented are the ranges of values for four pen and lot manure samples obtained from commercial feedlots in the Hereford-Dimmitt area. Except for having lower moisture contents, the experimental manures appear to be representative of High Plains cattle feedlot manures.

Table 2. CHARACTERIZATIONS OF FEEDLOT CATTLE MANURES

	Experimental feedlot manures		Commercial feedlot manures
	"A"	"B"	
Moisture content (weight percent)[a]	9.6	7.6	15.3 - 36.7
Ultimate analysis (weight percent)[b]			
Carbon	42.6	39.7	35.1 - 39.6
Hydrogen	5.5	4.8	5.3 - 5.9
Nitrogen	2.8	2.9	2.5 - 3.1
Sulfur	-	0.5	0.4 - 0.6
Ash	24.9	26.6	23.5 - 29.2
Heating value (kg cal/kg)[b,c]	3528	3256	3194 3739

[a] As received basis

[b] Dry basis

[c] Gross

SECTION V

DISCUSSION OF RESULTS

Bench-scale, fluidized-bed, partial oxidations of feedlot cattle manures were conducted to investigate the feasibility of transforming this solid waste to ammonia synthesis gas. Bottom feeding of manure to the reactor was initially selected in an effort to obtain full use of the unique advantages of the fluidized bed. Bottom-fed manure particles would be rapidly heated by a hot, back-mixed bed and would be forced to have some residence time in the bed before being entrained from the reactor. Although numerous attempts were made, this mode of feeding was never fully established at the laboratory scale. Something as simple as a few hairs bridging across the manure transport line was enough to cause plugging of this line and terminate operation. The first 32 runs in this series were mostly total failures with perhaps 3 or 4 very partial successes.

Little information was gained from the bottom-fed runs because mechanical operability was the primary concern. Although top feeding presented other problems, it was a reliable means of admitting manure to the heated environment of the reactor, and the six top-fed runs discussed in this chapter offer considerable insight into ammonia synthesis gas from manure. First, discussion of the overall aspects of the partial oxidations will be given.

PARTIAL OXIDATION RUNS

The operating conditions and some important results of the top-fed partial oxidations are presented in Table 3. As indicated, a significant feature of operation was the sometimes large temperature gradients within the reactor. Although the upper reactor temperature was constant during a run because the upper reactor thermocouple was the sensor for the furnace controller and variations in the lower reactor temperature were small to moderate (± 15° C), the absolute instantaneous difference between the two temperatures ranged up to 99° C. Such temperature gradients are not to be expected in a fluidized bed; the large inventory of solids in violent agitation that characterizes the fluidized bed creates a thermal flywheel resulting in isothermal operation.[21] Except during Run 5 and during a part of Run 2, the upper section of the reactor was at a lower temperature. A "cold" upper section would suggest that the top-fed manure was creating a heat load which could not be absorbed by the available bed. The greatest temperature differences occurred during Run 1 in which the manure rate of 0.5 kg/hr was more than twice as high as the feed rate in any other run.

Although the CO_2, which was passed through the manure feed line, did aid in transporting char from the bed, this stream was not considered to contribute to fluidization. The fluidization velocity was to be the sum of the steam and the product gas superficial velocities. (The product gas is the exit gas free of the added CO_2 and water vapor; the pyrolysis gas is the product gas free of N_2 and O_2.) The fluidization velocity was set at from 0.29 m/sec to 0.40 m/sec in the 6 successful top-fed runs.

An earlier attempt to fluidize with a velocity of 0.11 m/sec was unsuccessful as no char was entrained from the reactor until the latter

Table 3. SUMMARY OF THE PARTIAL OXIDATIONS OF MANURE

Manure fed	Run 1 "B"	Run 2 "A"	Run 3 "A"	Run 4 "A"	Run 5 "A"	Run 6 "A"
Reactor temperatures (°C)						
Upper	686.1	696.1	715	730	775	777.8
Lower	770 (±15)	690 (±6)	727.2(±2.7)	782.8	757.1(±2.2)	813.9(±7.2)
Mean	728	693	721	757	766	797
Superficial velocities (m/sec)						
Steam	0.17	0.34	0.24	0.25	0.25	0.21
Product gas[a]	0.23	0.05	0.07	0.12	0.09	0.08
Total	0.40	0.39	0.31	0.37	0.34	0.28
Material balance: Inputs (kg/hr)						
Wet manure	0.403	0.159	0.164	0.212	0.147	0.107
Air	0.095	0.039	0.039	0.039	0.039	0.039
Steam	0.150	0.330	0.225	0.225	0.225	0.180
CO_2	0.040	0.020	0.020	0.020	0.020	0.020
Total	0.748	0.548	0.448	0.496	0.431	0.346

Table 3 (continued). SUMMARY OF THE PARTIAL OXIDATIONS OF MANURE

Manure fed	Run 1 "B"	Run 2 "A"	Run 3 "A"	Run 4 "A"	Run 5 "A"	Run 6 "A"
Material balance Outputs (kg/hr)						
Total gas	0.314	0.088	0.112	0.168	0.121	0.119
Net char	0.101	0.070	0.076	0.109	0.085	0.058
Condensates	0.231	0.363	0.226	0.201	0.221	0.084
Bed accumulation	0.045	0.021	0.026	0.019	. .	0.012
Total	0.691	0.542	0.440	0.497	0.427	0.273
Percent recovery of mass	92.4	98.8	98.3	99.2	>99.2	80.0

[a]Excludes added CO_2.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Average product gas yield[a] (ℓ at 0° C and 1 atm. kg dry, ash-free manure fed)	807	603	721	862	975	1229

Table 3 (continued). SUMMARY OF THE PARTIAL OXIDATIONS OF MANURE

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Average product gas analysis[a,b] (volume percent)						
H_2-by difference	25.6	26.2	20.0	18.1	26.7	24.2
CO	16.4	12.6	14.3	15.4	17.3	11.5
CO_2	18.3	13.1	20.1	21.4	14.7	18.7
CH_4	7.3	6.2	7.8	7.9	6.4	6.8
C_2H_4	2.7	2.7	3.3	4.1	3.5	3.7
N_2	28.4	38.3	34.0	30.7	31.0	34.5
O_2	1.4	0.9	0.4	2.5	0.3	0.6
Char analysis (weight percent)[c]						
Moisture	. .	43.2	62.9	55.0	. .	62.7
Carbon	. .	40.4	41.2	36.4	. .	32.0
Hydrogen	. .	1.4	1.0	0.3	. .	1.6
Nitrogen	. .	2.5	2.5	2.4	. .	2.0
Ash	. .	36.7	39.5	. .	. .	53.9
Dry char heating (Btu/lb)	. .	5535	5502	. .	. .	4132

Table 3 (continued). SUMMARY OF THE PARTIAL OXIDATIONS OF MANURE

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Dry bed analysis (weight percent)						
Carbon	. .	. .	20.8	10.5	. .	. .
Hydrogen	. .	. .	0.7	~0	. .	. .
Nitrogen	. .	. .	0.7	0.2	. .	. .
Ash	. .	. .	87.5	98.7	. .	. .
Total condensate characteristics (mg/l)						
Chemical oxygen demand	. .	40925	35800	47000	. .	. .
Total solids	. .	12868	15830	30930	. .	. .
Volatile TS	. .	12433	14915	29150	. .	. .
Fixed TS	. .	570	2010	11595	. .	. .
Suspended solids	. .	450	1955	11180	. .	. .
Fixed SS	. .	120	55	415	. .	. .

[a]Excludes added CO_2.

[b]Average of 3-4 gas samples except Run 4 where only one gas sample was taken.

[c]Dry basis, except for percent moisture which is on a wet basis.

part of the run when raw, unpyrolyzed manure was carried over to the char collector. An examination of the reactor showed that a fixed, non-flowing bed had built up to the dip-tube level.

The higher velocities which were found to be required for successful operation were not entirely consistent with fluidization theory. A correlation, given by Kunii and Levenspiel[24] and due to Wen and Yu, was used to estimate the minimum fluidization velocity. For 40 - 60 mesh char particles of density 256.8 kg/m^3 this correlation predicts a minimum fluidization velocity of .0024 m/sec if the fluidizing gas is steam at 704.4° C. The char density was estimated by combining the experimental observation that a particle retained only about 20% of its mass in being transformed from wet manure to dry char with a reported literature value of 642.0 kg/m^3 for compacted manure containing 10% moisture.[2] With the same set of conditions a graphical correlation, again given by Kunii and Levenspiel[24] but due to Pinchbeck and Popper, predicts that char entrainment from the 4.1-cm ID reactor would begin at a velocity of 0.18 m/sec. The higher velocities that were set in the successful runs led to increased char entrainment, but entrainment was necessary as it provided the only means of egress for the reacted solids. These velocities were about 150 times greater than the estimated minimum velocity of 0.0024 m/sec for char particles. However, examinations of the bed materials did show the bed particles to be agglomerates of from five to ten char-sized particles. The experimental fluidization velocities were at least ten times the minimum for these agglomerates.

There was no evidence that ash fusion was the cause of these easily crushed agglomerates. The beds often contained 0.64- to 1.3-cm agglomerates which were ashen in appearance. Some, but not all, of these larger agglomerates are believed to have arisen from the infrequent use of the ram to clear the manure feed line of plugs. The formation of these unfluidized particles may have contributed to the plugging problems encountered in the bottom-fed runs.

The steam flow in the top-fed runs was used more as a means of setting the fluidization velocity than as a reactant. The use of steam arose from the belief that the problems with bottom feeding were due, in part, to irregularities in the manure feeding. The star feeder inherently dumped discrete batches of manure into the transport line leading to the base of the reactor. When, as in the bottom-fed runs, the gas evolved from manure constituted the bulk of the gas within the reactor, the bed could collapse between "slugs" of highly reactive manure. The high reactivity of the manure was evidenced by the observation that surges of vapors to the condensate collection flasks were in phase with the batches of manure dumped from the feeder. The high reactivity of manure was further evidenced by the 90% ash content of one bottom-fed bed. Therefore, to dampen the effects of intermittent feeding and stabilize the gas velocity within the reactor a steady flow of steam was added to the airflow. The steam was generated under the system back-pressure of no more than 25.4 cm H_2O and carried little superheat. It should be emphasized that it is not anticipated that such a large amount of steam would be required at a larger scale. Its use was principally due to the scale of the reactor system.

The effects of steam addition to a partial oxidation reaction must be considered. Experiments with municipal solid waste (MSW) have shown that the steam-carbon reaction, the steam-hydrocarbon reactions, and the water-gas shift reaction all take place, and appropriate shifts in the product distribution have been observed. The endothermic steam-carbon and steam-hydrocarbon reactions were used to explain increased water consumption as the pyrolysis temperature was increased from 482.2° to 982.2° C.[31] However, the consumption of water was low and relatively constant at about 5 kg H_2O/100 kg MSW at temperatures below 815.6° C. The water consumption did increase drastically to about 13.6 kg/45.5 kg between 815.6° and 982.2° C . Studies made with coal char have shown that the rate of the steam-carbon reaction is quite low at temperatures below 926.7° C.[32] The use of steam is not, then, thought to have led

to increased production of ultimate hydrogen (H_2 + CO) in the lower temperature runs of this study.

As shown in Table 3, the total output of gas condensates and char was not sufficient to account for the total input of mass. Accumulation of solid material in the bed accounted for the remainder. The runs were, then, not strictly steady-state runs, but, if a bed remains inert, such accumulations will not lead to transients in the various product rates and compositions. The beds of Runs 3 and 4 were found to be largely inert ash. These bed analyses each sum to greater than 100% because a portion of the total carton given in the C-H-N analysis remains as inorganic carbonate carbon in the residue of the ash determination.[33] A bed analysis is probably not the true inrun bed composition because the reactor had to be cooled before bed samples could be taken. Devolatilization of the bed material could have occurred during the initial states of this cooling period. However, as previously alluded to, the high inertness of, or lack of, the beds was evidenced by imperceptible gas generation during periods of no manure feeding. Despite accumulation in the beds, the bed material collected from the one- to two-hour runs weighed no more than 22 to 47 grams. The expanded beds during a run were then quite dilute. Dilute beds would be consistent with large temperature gradients within the reactor and with fluidization velocities which were theoretically high.

The solids characterizations showed the chars to be considerably less inert than the beds. The chars had heating values of 7167 to 7611 kg cal/kg of total carbon in the char. These heats of combustion compare with that of graphite carbon at 7833 kg cal/kg. As the carbon exiting with the char ranged from 16.8% to 26.2% of the carbon in the manure fed, substantial portions of the incoming combustion energy were unutilized in the reactor. There was some concern, due to the high reactivity of the manure and the dilute beds obtained, that the top-fed manure particles were being entrained from the reactor by the gas evolved from the manure itself before being completely pyrolyzed. However, the yields of ash-free char were,

in fact, lower than those of prolonged batch pyrolyses of manure that are reported in the literature (See Table 1). Apparently, the reactor with its large surface-to-volume ratio was being supplied with enough heat from the furnace coils to compensate for the lack of bed material. For unheated reactors much greater amounts of hot, back-mixed bed material will undoubtedly be required to obtain the fast heating rates simulated in these experiments.

As shown in Table 3, high strength condensates were produced by the process. It should be noted, however, that excessive amounts of steam were employed in order to stabilize the fluidization in the reactor, an unnecessary operation for larger reactors, thus accounting for the relatively large volumes produced. Nonetheless, significant volumes of high strength condensates will be produced and must be handled effectively.

From Figure 7 it is seen that at 801.67° C, the anticipated Phase II reaction temperature, about 70% of the product carbon is in the gas and solid phases, leaving 30% in the liquid or condensate phase. If it is assumed that the manure as received contains 40% carbon on a dry weight basis and 20% moisture, that all the carbon containing condensates are alkanes weighing 960 kg/m^3, that all the water in the manure exits the reactor, and that 0.1 kg steam/kg manure will be required, then approximately 41.2 kg or .041 m^3 of condensates will be produced per 100 kg of manure reacted. Referring to the previously mentioned Hereford area with a capacity for feeding 600,000 cattle/day, about 953.8 m^3 of condensate will be produced daily.

Because of the exceedingly high organic strength of the condensate, conventional treatment of this emulsified waste would prove inadequate. Therefore, stage condensation will be employed in Phase II to collect the condensible by-products in relatively pure states. These will then be recycled or marketed as heating fuel. The water, approximately 696.44 m^3,

can be utilized for steam production, treated, if necessary, and used for irrigation purposes, or permanently impounded and allowed to evaporate.

AMMONIA SYNTHESIS GAS FROM MANURE

The stated goal of this study was to determine the feasibility of producing a gas suitable for the synthesis of ammonia from cattle manure. The yields and compositions of the product gases were then of primary importance in this work.

As expected, the gases evolved from manure were composed largely of H_2, CO, CO_2, and CH_4. The unsaturated hydrocarbon ethylene (C_2H_4) was the only other gas of pyrolysis present in sufficient concentration to be detected in the routine gas analysis. The percentage of methane in the N_2- and O_2-free pyrolysis gas was essentially constant as it ranged only from 9.3 to 11.9. The ethylene concentration in the pyrolysis gas followed no trend during the course of the runs but ranged from 3.8 to 6.1 volume percent. The gas from the fluidized-bed pyrolysis of manure at 760° C by Bailie[25] contained 7.7% CH_4, 1.9% C_2H_4, and 0.3% C_2H_6; however, the low temperature, batch pyrolysis of Garner and Smith[11] contained more ethane (C_2H_6) than ethylene. In Runs 5 and 6 the routine gas analysis was supplemented with a semi-quantitative, hydrocarbon gas analysis given by a chromatograph equipped with a hydrogen flame ionization detector. All samples were shown to have ethane and propylene in amounts less than 10% of the ethylene.

In Figure 4 are presented the yields of ultimate hydrogen obtained directly from the partial oxidations of manure. The ultimate hydrogen yield was defined as the sum of the pound moles of H_2 and CO produced per pound of dry, ash-free manure fed to the reactor and is plotted versus the mean reactor temperature. Carbon monoxide was considered to be hydrogen in that it directly results from the partial oxidations because, in a conventional

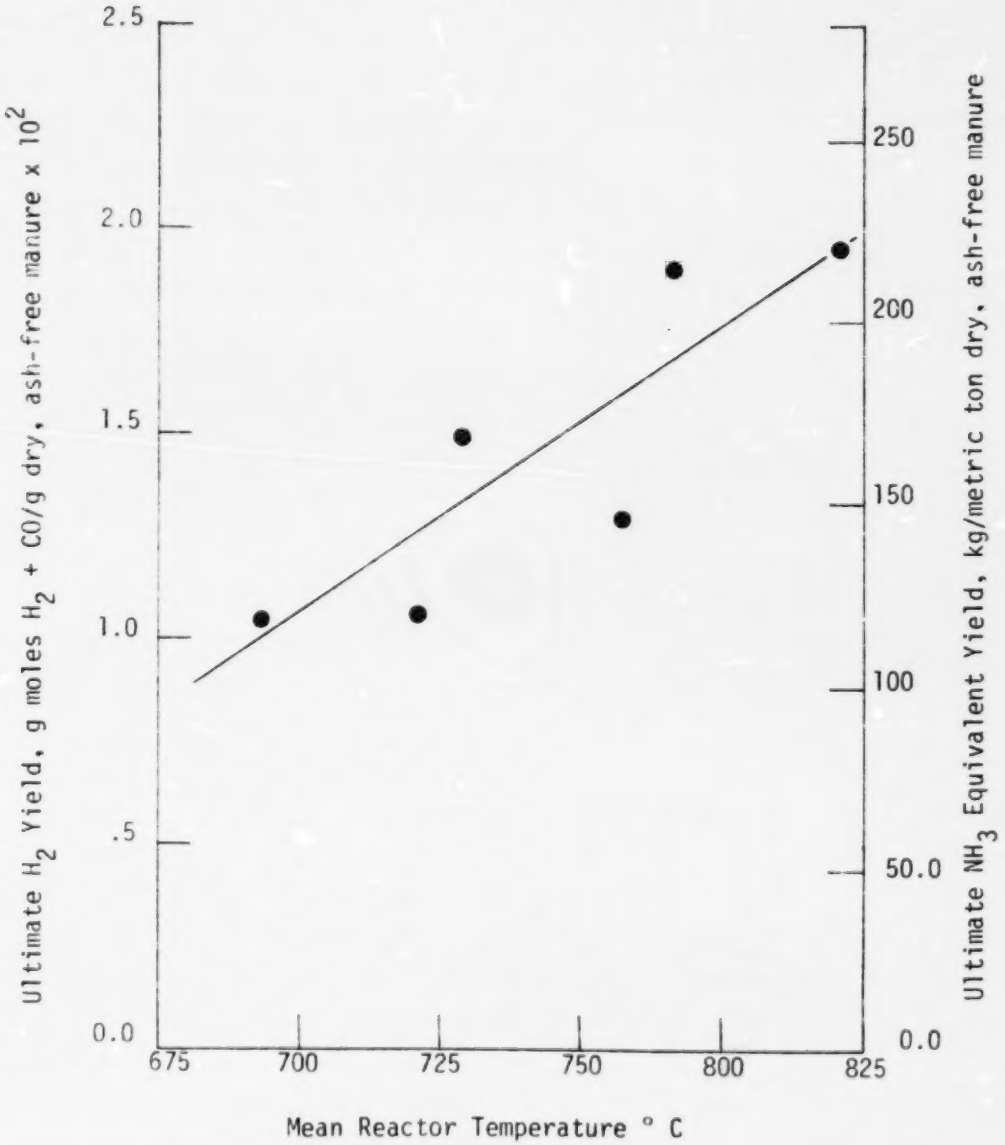


Figure 4

Ultimate hydrogen yield from manure
(before reforming)

ammonia plant, CO is shifted to H_2 via the water gas reaction:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad (1)$$

The reactor temperature, since it fixes the heating rate to particles of a given size, was expected to be a significant variable. The mean reactor temperature, which is the arithmetic average of the upper and the lower reactor temperatures, was found to be the best means of correlating the various yields of all runs. Although this means of data correlation led to considerable scatter, higher temperatures are shown to result in greater yields of ultimate hydrogen. On a per kg of dry, ash-free manure basis, the ultimate hydrogen yield increased from 19.1 to 35.9 kg over the 90° C range investigated. Again on a per kg basis, the ammonia equivalent of the ultimate hydrogen yielded is from 108.2 to 203.2 kg.

Of course, a variable in addition to the reactor temperature which could have influenced the yields of any combustible gas was the amount of air added to the partial oxidation reaction. The relative air rate in these runs did range from 0.27 to 0.53 kg air/kg dry, ash-free manure fed. However, the highest relative air rate was in Run 6 in which the highest yields of all combustible gases were realized.

As shown in Figure 5, the yields of the hydrocarbons, methane and ethylene, were well correlated by the mean reactor temperature. The yield of each of these hydrocarbons more than doubled as the mean reactor temperature was raised from 693.3° to 795.6° C.

The results of these bench-scale partial oxidations can be put on basis more meaningful for commercial process development when the basic technology of ammonia plants is considered. A synthesis gas that is introduced as make-up into an ammonia synthesis loop must be relatively free of inerts to avoid product loss to purge. All hydrocarbons are inerts

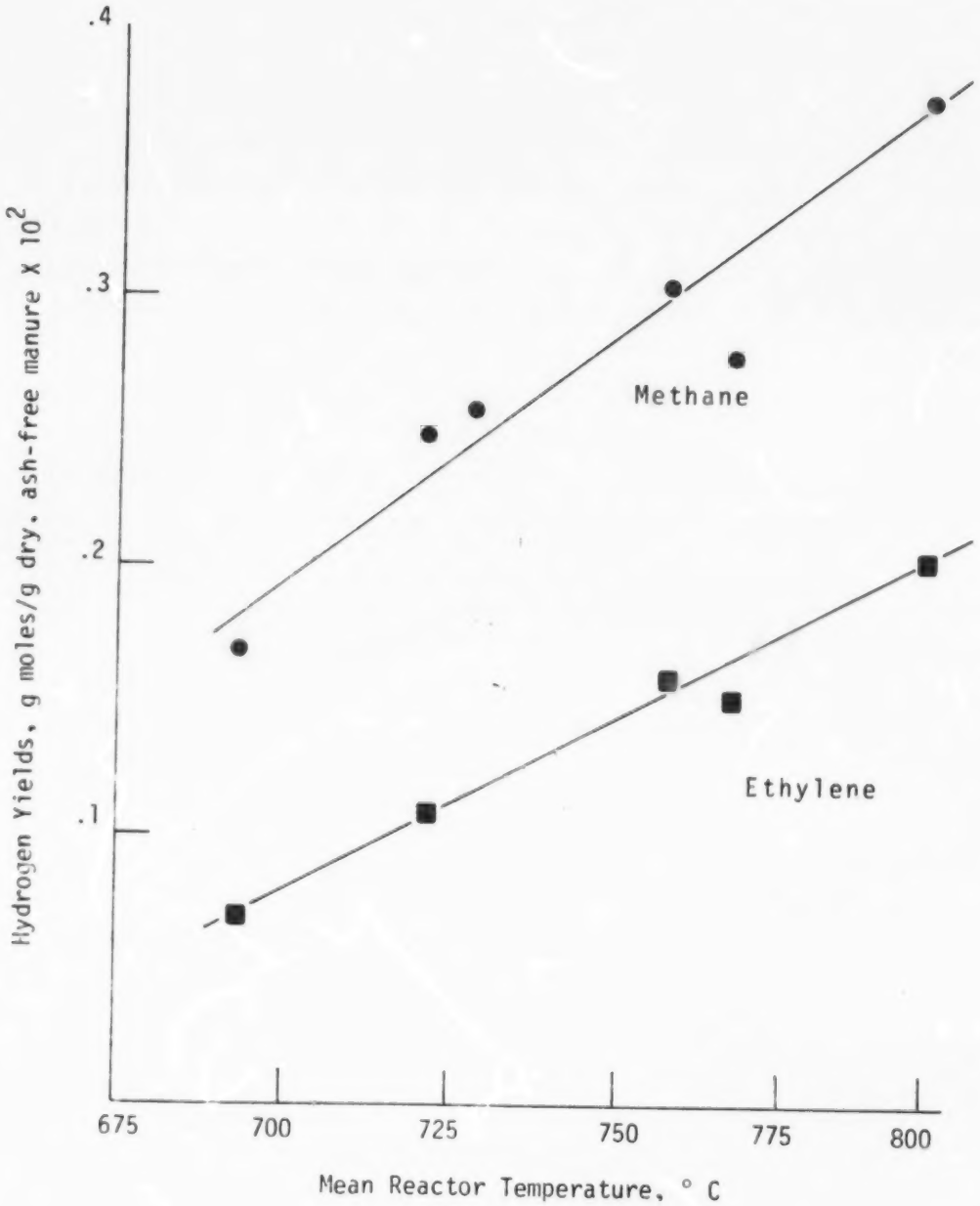


Figure 5

Hydrogen yields from manure

in ammonia production. A process log sheet provided by a local ammonia producer[34] shows that the make-up synthesis gas contains less than 0.5% CH_4 and no other hydrocarbons. The high hydrocarbon contents of the experimental product gases would make these gases unacceptable to a conventional ammonia plant.

Excess nitrogen in a synthesis gas is undesirable because reacted nitrogen remains in the synthesis loop unless purged. Ammonia synthesis gas normally contains no less than the stoichiometric ratio of 3 moles H_2/mole N_2. The H_2 + CO to N_2 ratios of the experimental gases were unacceptably low. These synthesis gas ratios were all less than 1.5:1.

A logical means of increasing the synthesis gas ratio, while, at the same time, purifying the gas from hydrocarbons, would be to thermally reform, with steam, the gas of partial oxidation. The steam reforming of methane and ethylene would produce ultimate hydrogen through the reactions:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (2a)$$

and

$$C_2H_4 + 2H_2O \rightleftharpoons 2CO + 4H_2 \qquad (2b)$$

With each mole of methane and ethylene yielding four and six moles, respectively, of ultimate hydrogen via steam reforming, the synthesis gas ratio could be increased significantly by the application of these reactions.

The aspects of steam-hydrocarbon reforming have been discussed elsewhere.[35, 36, 37, 38] The aspect that would appear to most limit the usefulness of reforming the gas from manure is the low sulfur requirement. The total sulfur in the gas to a reformer must be less than 0.5 parts-per-million (ppm) to avoid frequent regeneration of the nickel catalyst. Spot determinations of the sulfur content of the exit gases of Runs 5 and 6 were

made using Kitagawa H_2S Detector Tubes. The H_2S concentration in the added CO_2-free product gas ranged from 232,000 to 294,000 ppm.

Although it was recognized that a desulfurization step must, in practice, precede a catalytic reformer, reactions (2a) and (2b) were used to conceptually convert the experimental yields of hydrocarbons to H_2 and CO. The sum of the ultimate hydrogen resulting from the reforming reactions and that yielded directly from manure constitutes the projected ultimate hydrogen from manure. These projected ultimate H_2 yields are plotted versus the mean, bench-scale, reactor temperature in Figure 6. The mean temperature is shown to be an excellent means of correlating these projected H_2 yields. On a per 909 kg of dry, ash-free manure basis, the projected ultimate hydrogen yield increased continuously from 39.1 kg at a mean temperature of 693.3° C. The upper yield is equivalent to 486 kg of ammonia.

Despite the fact that the char analyses were consistent with reported batch pyrolyses of manure, there was some concern, due to the rather ill-defined state of fluidization, that these projected yields would not be representative of those from future fluidized beds. However, as shown in Figure 6, the projected yield calculated from the results of the pilot-scale, fluidized-bed pyrolysis of manure by Bailie[25] is very consistent with the bench-scale data. This only indicates that this study was consistent with other small-scale experiments. Scale up of these data to larger-scale systems will require additional experimentation.

Synthesis gas ratios of the experimental product gases would be increased by factors greater than two if these gases were to be reformed. Table 4 gives the synthesis gas ratios of the gases as they exited the bench-scale reactor and the projected synthesis gas ratios if the gases were to be passed through a catalytic reformer to convert the methane and ethylene to ultimate hydrogen. It should be emphasized that this ratio may be easily manipulated by changing reactor conditions.

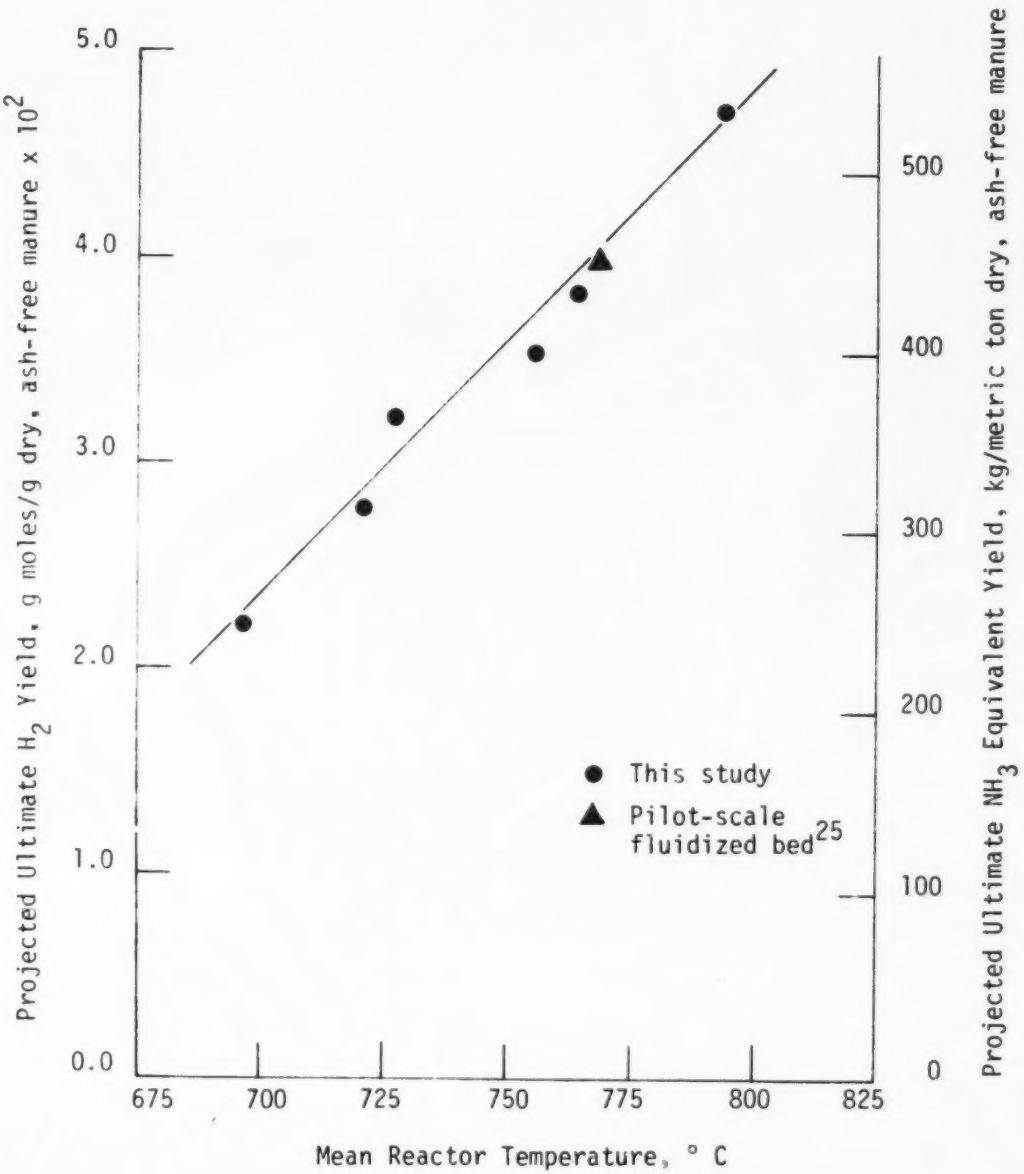


Figure 6

Projected ultimate hydrogen yield from manure (after reforming)

Table 4. SYNTHESIS GAS RATIOS OF THE PRODUCT GASES

Ultimate H_2:N_2	Run Number 1	2	3	4	5	6
Before reforming	1.5	1.0	1.0	1.1	1.4	1.1
After reforming - based on gas analysis	3.1	2.1	2.5	2.9	2.9	2.5

The projections given in Table 4 do show that, if reformed, the experimental product gases would have, in general, synthesis gas ratios consistent with conventional ammonia technology. Of course, the ratios could have been increased or decreased simply by adjusting the amount of air added to the pyrolysis reactions.

The partial oxidations which have been conducted show no limit to the amount of ultimate hydrogen that can be projected from manure. Greater insight into the situation of gas production can be had from Figure 7 which gives the carbon distribution between the gaseous and solid products of partial oxidation as a function of the mean reactor temperature.

Increased temperature definitely shifts the carbon distribution toward the gas. However, at no temperature is more than 67% of the carbon that was fed in with the manure accounted for by the gas and the char analyses. It was assumed that the remaining carbon left the system in the form of oils and tars. Since these tended to coat the transfer lines, it was almost impossible to accurately measure the amounts generated.

The amount of carbon appearing in the gas phase increased by over 30 percentage points as the mean reactor temperature was raised from 693.3° to 795° C, and the amount of carbon remaining in the char decreased by less than 10 percentage points. These facts, taken together, suggest that increased rates of secondary reactions involving the higher hydrocarbons that normally condensed in the recovery train were the primary sources of increased gas production at the higher temperatures. The yields of gas from secondary reactions could be increased by raising the temperature or by lengthening the gas residence time in the reactor. The reverse of the latter was done by Garner and Smith[11] who sought to maximize the production of liquids by quickly removing the primary products of pyrolysis from the heated environment.

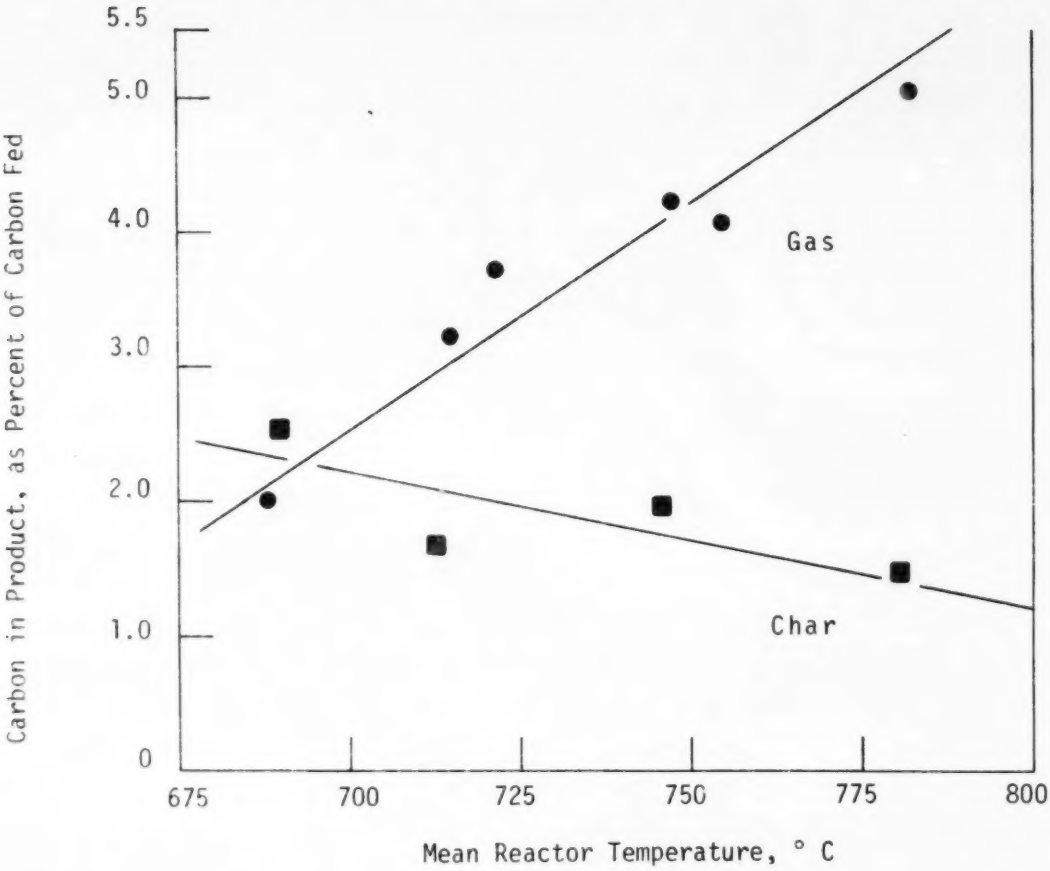


Figure 7

Carbon distribution between gas and char

Since chars and condensates constituted considerable portions of the products of the partial oxidations, and since the gases of partial oxidation contained hydrocarbons, it is to be expected that the energy requirements for these conversions would be less than that for the complete conversion of the reactive portion of the manure to ammonia synthesis gas. The energy requirements were estimated for each of the four runs in which the characteristics of the chars were known. Tentative energy balances for these runs are presented in Table 5. Each balance assumes that the steam fed to the reactor was saturated at atmospheric pressure, and, for the purposes of estimating the latent and sensible energies, that the condensible fraction of the vapors exiting the reactor had the properties of steam at the upper reactor temperature. For the condensible vapors, the gross heat of combustion in the condensed state which is listed as the chemical energy was assumed to be 7628 kg cal/kg of carbon. This latter assumption has given closure to a previous energy balance involving a pyrolysis of municipal waste.[17] The carbon content of the condensible vapors was determined by difference.

The reported chemical energy of the manure and of the char is the measured gross heat of combustion for that particular solid. Since this quantity was not measured, the char of Run 4 was assumed to have a gross heat of combustion of 7222 kg cal/kg of total carbon in that char.

The specific heat of each char was assumed to be 0.3 kg cal/kg° C. Finally, the gross heats of combustion of the product gases, which are the chemical energies of those gases, were calculated from the gas analyses and tabulated combustion data.

Because the estimated contributions of the vapors are large, the energy balances can be considered as only approximately, but they do give indications. Although the net energy requirements of the partial oxidations are relatively larger, the combined chemical and latent energy effects, which

Table 5. ENERGY BALANCES
(kg cal/kg, ash-free manure fed)

	Run Number 2	3	4	6
Inputs:				
Manure				
Chemical energy	4697	4697	4697	4697
Sensible energy	0	0	0	0
Latent energy	0	0	0	0
Steam				
Chemical energy	0	0	0	0
Sensible energy	229	152	117	186
Latent energy	1644	1094	841	1337
Outputs:				
Product gas				
Chemical energy	1312	1653	2059	2830
Sensible energy	191	237	279	431
Latent energy	0	0	0	0
Char				
Chemical energy	1131	777	858	684
Sensible energy	74	53	69	67
Latent energy				
Condensable vapors (estimated)				
Chemical energy	2277	2099	1562	1372
Sensible energy	1197	839	627	623
Latent energy	1965	1337	981	912
Combined chemical and latent energy effect	+ 342	+ 73	- 78	- 236
Sensible energy effect	+1232	+ 976	+ 858	+ 934
Net energy requirement	1574	1049	780	698

exclude the sensible energy losses from the reactor, are small. Even the most endothermic requirement of 342.2 kg cal/kg of dry, ash-free manure fed to the reactor is less than 8% of the chemical energy incoming with the manure. Considerable portions of the incoming chemical energy exits unutilized with the chars, and the recovery of this energy could make the net energy requirement of the partial oxidation reaction small.

SECTION VI

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